Inductive Effect of Substituents on the Symmetrical Methyl Deformation Frequencies of Aliphatic Hydrocarbons

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ABSTRACTS

Inductive Effect of Substituents on the Symmetrical Methyl Deformation Frequencies of Aliphatic Hydrocarbons

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In order to discuss the inductive effect of polar group upon methyl group in a molecule, the symmetrical methyl deformation frequencies δ_{CH_3} of $CH_3(CH_2)_{n-1}XH_{m-1}$ molecules were measured, where X represents an atom in groups IV~VII of the periodic table, m the valence of X atom and n the carbon number of the molecule.

For CH_3XH_{m-1} molecules ($n=1$), a linear relationship was found to exist between the frequency and logarithm of the electronegativity x_X of X atom for each row and column of the periodic table. These frequency variations are ascribed to change in the deformation force constants, and can be expressed as

$$\delta_{CH_3}=375\log\left(\frac{x_X}{r^2_{CX}}\right)+1366$$

where r_{CX} is the C-X bond length. This equation holds not only for CH_3XH_{m-1} molecules but also for the series $(CH_3)_2XH_{m-2},\cdots\cdots(CH_3)_mX$ within the error of $\pm 1\%$.

Frequency variations due to the change of the carbon number of $CH_3(CH_2)_{n-1}XH_{m-1}$ molecule ($n\geqq 2$) can be interpreted by a modified equation in which the factor $\{(x_C+0.40\varepsilon_X\sigma^{n-2})/r_{CC}^2\}$ is used instead of (x_X/r_{CX}^2) in the above equation. Here, r_{CC} is the C-C bond length, x_C the electronegativity of carbon atom, ε_X the induced charge on the carbon atom adjacent to X atom, and σ the ratio of the induced charges at any two adjacent carbon atoms in the alkyl chain.

Dielectric Properties of Emulsions. (III) Dielectric Behavior of W/O Emulsions

Tetsuya HANAI

Kolloid Zeitschrift, 177, 57 (1961)

Dielectric constants and electrical conductivities of W/O emulsions at rest and under shear were measured over a wide range of concentration and at frequencies ranging from 20 cps. to 5 mc.

Striking dielectric dispersions due to the interfacial polarization were observed at high frequency range above 100 kc., while the electrode polarization was found below 1 kc.

It was found that the dielectric dispersions due to the interfacial polarization